

# Scanning Tunneling Spectroscopy of Field-Induced Au Nanodots on Ultrathin Oxides on Si(100)

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We present tunneling spectra for nanometer scale Au dots on in-situ oxidized Si(100). The spectra were measured for dots fabricated on clean and oxidized surfaces for oxide thickness from zero to 1 ML. Two important features are observed. First tunneling IV spectra of the dots on the atomically clean surfaces show metallic behavior, confirming the identification of the dots as deposited Au from the tip. Second, tunneling spectra from Au dots on the partially oxidized surfaces show a feature at approximately 2V (sample positive) with weak negative differential resistance (NDR). We associate this feature with oxide related defect sites which we observe at densities that increase from 0.06 to 0.3 /nm<sup>2</sup> as oxide coverage increases from 0.1 to 1 ML. The probability of observing this feature through a gold dot increases by about a factor of 2, suggesting that the dot increases the effective sampling area of the defect sites by the same factor.

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Scanning Tunneling Microscopy (STM) is by now well established as a powerful tool for characterization and modification of nanometer scale structure [1-3]. The associated capability of probing local electronic structures with Scanning Tunneling Spectroscopy (STS) has allowed the intensive study of the electronic states of metals [4-5] and semiconductors [6-8]. Recently, investigations of the electronic structure of field-induced nanostructures have attracted much attention from the viewpoint of the fundamental study of electron transport as well as the technical application of nanoelectronic devices [9-12].

Tunneling through metal dots supported on an insulating layer has been suggested as a method of creating room-temperature Single Electron Tunneling (SET) devices [9-11]. However, as was earlier demonstrated by Koch and Hamers [13-15], thin oxide layers act not only as insulating layers, but also introduce features in the tunneling spectra with time-dependent (noisy) properties. Koch and Hamers attributed these features to charge trapping at defect states in the oxide. Reports [9,10] of oscillations in IV characteristics of metallic nanodots on a silicon oxide substrate have recently been demonstrated to result from a specific time dependence rather than a voltage dependence [12], and thus are not the result of SET behavior. Instead, the temporal behavior has been associated with charge-discharge effects at electron traps [12].

Previously we have reported on the variation with oxide coverage of the threshold field for producing Au nanodots on an oxidized Si(100) surface [16]. In this study, we present tunneling IV spectra from this system. We find evidence for metallic behavior and for I-V characteristics associated with charging of interface trap states. The spectral

feature associated with this latter observation is observed in direct tunneling through the oxide and with higher probability when tunneling through Au dots deposited on the oxide. We interpret the increased probability as due to an increase in the effective area of the defect when sampled at the metal-oxide interface.

The STM setup and sample preparation have been described in detail elsewhere [16]. The experiment was performed with a commercial STM (Park Scientific Instruments Autoprobe VP) in a vacuum chamber with a base pressure of  $1.0 \times 10^{-10}$  torr. Tungsten STM tips were first electrochemically etched, then Au coated by thermal evaporation.

The silicon samples were n-type (20x10x0.5 mm, P-doped, 2-3  $\Omega\bullet\text{cm}$ , (100) orientation  $\pm 0.1^\circ$ ). These were electrochemically etched using the Shiraki method [17], then heated to approximately 1250 °C using electron beam bombardment in vacuum. After cooling the sample slowly at rates of 2 °C/s [18], the Si(100) dimer row reconstruction could be imaged with the Au-coated tip. Due to the nonreactive nature of the Au coating, the tunneling characteristics were quite stable. We subsequently oxidized the Si surface by exposing to pure (99.99 %) O<sub>2</sub> at a pressure of  $2.0 \times 10^{-7}$  torr for various doses. The sample was held at room temperature during the dose. We estimate the oxide thickness using a published calibration of the sticking coefficient of oxygen on the Si(100) as a function of temperature [19,20].

For the Au transfer, we applied voltage pulses (pulse magnitude between  $\pm 10$  V, and pulse widths of 0.1-100 ms) to the sample while monitoring the tunneling current. During the application of pulses, the feedback was switched off to keep the tip-sample

distance nearly constant. The typical diameter of a gold dot formed by this technique was 3~20 nm with a height between 0.4 ~ 2 nm. The sizes were strongly dependent on the magnitude and polarity of the pulse. Figure 1(a) shows an image of a 3 nm diameter gold dot made on a Si(100) dimer row reconstructed surface formed by a  $-7$  V, 100 ms pulse. Also in Fig 1(a), atomically resolved features are observed after dot formation, indicating that the STM tip regenerates to a sharp tunneling tip.

An STM image of a second dot, fabricated on a clean Si (100) surface, and the corresponding normalized conductance spectra are shown in Fig. 1(b) and Fig. 1(c). The latter were measured with sweep time of 150 ms and with 10 spectra averaged. The normalized conductance ( $dI/dV/(I/V)$ ) taken on the top of the dot (position “A”) is plotted as open squares and shows little or no surface state band gap. This suggests that the Au-Si bond has introduced surface states in the semiconductor energy gap, resulting in near-ohmic contact between the dots and the silicon substrate [4]. For comparison we also measured the tunneling spectrum over the dimer row region (position “B”), which is plotted as the solid curve. The corresponding normalized conductance in this case shows a surface state bandgap of  $\sim 0.7$  eV, consistent with the semiconducting nature of the Si(100) dimer row reported elsewhere [7,8].

The conductance spectrum taken over the dot allows us to exclude the possibility that the dots result from field induced migration of Si during the pulse, as might be suggested by the observation by Ichiyama et al. of field-induced mound formation on Si at elevated substrate temperature [21]. The metallic conductance spectrum indicates instead that the material in the dot modifies bands at the interface and thus is not Si, but Au, or a Au alloy [4]. Our measurement thus supports the model of field induced

fabrication as due to direct Au transfer from the tip to the sample, which was also confirmed by other surface sensitive techniques such as Energy Dispersive X-ray Spectroscopy (EDX), and Field Emission Scanning Auger Microscopy (FESAM) [22,23].

Figure 2(a) shows an STM image of a Au dot on a partially oxidized Si surface ( $\sim 0.2$  ML), formed during a  $-8$  V, 100 ms pulse. In this case, the diameter is 7 nm, and the height is 1.0 nm. Again, the dimer row structure is visible on the surrounding unoxidized parts of the surface indicating an atomically sharp tip, although no ordered structure is observed at the dot surface. Isolated bright spots on Si dimer row can be attributed to the ejection of Si atoms during the early stage of oxidation [8].

Averaged spectra from some of the dots do show interesting voltage dependent features. An example can be seen in Fig 2(c) which was measured above the dot imaged in Fig 2(b). The normalized conductance, shown in the inset again shows little or no energy bandgap, as well as a number of features not evident in Fig 1(c) [4]. The I-V spectrum shows a feature at a positive sample bias of about 2.2 V. The feature is a local maximum in tunneling current, showing weak negative differential resistance. To investigate if the observed feature is associated with the dot structure itself or with the underlying surface, we measured such spectra at a number of dots with diameter of 5-10 nm, as well as at a number of places on the oxidized surface. A summary of our measurements is shown in Fig. 3(a) and Table I. On the oxide surface, IV measurements were made after moving the STM tip sequentially to different, randomly chosen positions on the surface. On the surface with dots, sampling was performed at randomly chosen positions above the dots. When tunneling through the oxide directly, the probability of

observing NDR increases from about 5% to about 24% with increasing oxide coverage. The probability of observing NDR when measuring through the Au dots increases from about 7% to about 50% with increasing oxide coverage. At the lowest oxide coverages, the NDR spectral feature is observed for tunneling through only some of the dots. At the higher oxide coverages, the feature is observed for tunneling through all of the dots, but only at certain positions on each dot. The probability for observing the feature tends to be higher near the edges of the dots than in the center. This may be due to a redistribution of the field lines between the tip and the sample due to the induced charge distribution on the surfaces of the metal dot.

Both the nonzero probability of observing the NDR spectral feature away from the dots and the increase in the probabilities with oxide coverage in the submonolayer regime suggest that it is associated with tunneling through oxide interface states, as suggested by Koch and Hamers [13,14]. Because Koch and Hamers observed that such features were spatially correlated with regions in the oxide where substantial charge trapping noise was observed [13, 14], they concluded that the NDR feature was due to charge trapping. The charge trapping mechanism is illustrated schematically in Fig. 3b. Enhanced tunneling probability occurs when the applied voltage allows electrons to fill the charge trap. Once the trap is filled, coulomb repulsion lowers the tunneling probability leading to the observed NDR [13,14]. Xie and Blankenhagen suggested that this mechanism could explain oscillations in the tunneling probability which they observed at harmonics of 29.99 Hz [12]. When we measure IV spectra on the oxidized surface without averaging multiple scans, we observe oscillations with a frequency of multiples of 60 Hz, consistent with a noise-coupled mechanism.

From the probability of observing the NDR feature on the oxidized surface, we can estimate the areal density of the trapping states. Koch and Hamers estimated the STM-sampling-area for a defect site to have a diameter of 1 nm [13]. With this value, the probabilities listed in Table I roughly correspond to defect densities from  $0.06 \text{ nm}^{-2}$  at 0.1 ML of oxide to  $0.3 \text{ nm}^{-2}$  at 1 ML of oxide. The effect of adding the gold dots is to increase the probability of observing the NDR feature by about a factor of two for any given oxide thickness. If we assume no change in the density of trapping features beneath the dot, then the results indicate that the STM-sampling-area for detecting the influence of the dots is larger by about a factor of two for tunneling through the gold dot than for direct measurement on the oxide. We thus estimate the sampling area for defects measured through a gold dot to have a diameter of about  $2^{1/2} \text{ nm} \sim 1.4 \text{ nm}$ . This value is effective for Au dots with diameters of 5-10 nm. Large Au dots (>50 nm) yield a smaller probability of observing the NDR feature apparently due to near-ohmic contact to the substrate.

In summary, we have studied the electronic structure of field-induced fabricated Au dots on an in-situ grown oxide/ Si(100) surface. Tunneling spectra measured from dots on clean Si(100) surface confirm that the material of dot is Au rather than Si. Tunneling spectra on the oxidized surface occasionally show a spectral feature at approximately 2.2 V sample positive. This feature is most likely due to a electron trapping in a trapped charge state as proposed by Koch and Hamers [13,14]. The probability of observing this feature is enhanced for tunneling spectra measured through Au dots on the oxidized surface. We find evidence that the role of Au is that of an

efficient collector which enhances the tunneling into trap states buried at the Si /oxide interface.

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Table I. Ratio (number of observation of feature to the total number of measurements) and corresponding probability of observing negative differential resistance where the STM tip is positioned on the oxide and on the Au dots, respectively.

Thickness of oxide (ML)	oxide		Au dot	
	Ratio	Probability	Ratio	Probability
0.0	0/64	0.0	0/64	0.0
0.1	8/176	0.05	12/180	0.07
0.2	8/64	0.13	16/68	0.24
0.5	24/124	0.19	80/192	0.42
0.8	16/72	0.22	60/128	0.47
1.0	16/68	0.24	56/116	0.48

## REFERENCE

1. J. Stroschio, and D. Eigler, *Science* **254**, 1318 (1991).
2. I. -W. Lyo, and P. Avouris, *Science* **253**, 173 (1991).
3. A. Kobayashi, F. Grey, R. S. Williams, and M. Aono, *Science* **259**, 1724 (1993).
4. L. A. Gheber, M. Hershinkel, G. Gorodetsky, V. Volterra, *Appl. Phys. Lett.* **69**, 400 (1996).
5. Y. Kuk, and P. J. Silverman, *J. Vac. Sci. Technol.* **A8**, 289 (1990).
6. J. A. Stroschio, R. M. Feenstra, and A. P. Fein, *Phys. Rev. Lett.* **57**, 2579 (1986).
7. R. J. Hamers, Ph. Avouris, and F. Bozso, *Phys. Rev. Lett.* **59**, 2071 (1987).
8. D. G. Cahill, and Ph. Avouris, *Appl. Phys. Lett.* **60**, 326 (1992).
9. P. Radojkovic, M. Schwartzkopff, M. Enachescu, E. Stefanov, E. Hartmann, and F. Koch, *J. Vac. Sci. Technol.* **B14**,1229 (1996).
10. X. Hu, and D. Sarid, and P. von Blanckenhagen, *Nanotechnology* **10**, 209 (1999).
11. R. Houbertz, U. Weber, and U. Hartmann, *Appl. Phys. A* **66**, S149 (1998).
12. F. Xie, and P. von Blanckenhagen, *Appl. Phys. Lett.* **75**, 3144 (1999).
13. R. J. Hamers and R. H. Koch, in *The Physics and Chemistry of SiO<sub>2</sub> and the Si-SiO<sub>2</sub> Interface*, edited by C. R. Helms and B. E. Deal (Plenum, New York, 1988), p. 201
14. M. E. Welland, and R. H. Koch, *Appl. Phys. Lett.* **48** , 724 (1986).
15. R. H. Koch, and R. J. Hamers, *Surf. Sci.* **181**, 333 (1987).
16. J. -Y. Park, R. J. Phaneuf, and E. D. Williams, (to be published).
17. A. Ishizaki and Y. Shiraki, *J. Electrochem. Soc.* **133**, 666 (1986).

18. See, for example B. S. Swartzentruber, Y. –W. Mo, M. B. Webb, and M. G. Lagally, *J. Vac. Sci. Technol.* **A7** 2901 (1989).
19. T. Engel, *Surf. Sci. Rep.* **18**, 91 (1993).
20. J. Westermann, H. Nienhaus, and W. Mönch, *Surf. Sci.* **311**, 101 (1994).
21. A. Ichimiya, Y. Tanaka, and K. Ishiyama, *Phys. Rev. Lett.* **76**, 4721 (1996).
22. G. S. Hsiao, R. M. Penner, and J. Kingsley, *Appl. Phys. Lett.* **64**, 1350 (1994).
23. H. Koyanagi, S. Hosaka, R. Imura, and M. Shirai, *Appl. Phys. Lett.* **67**, 2609 (1995).

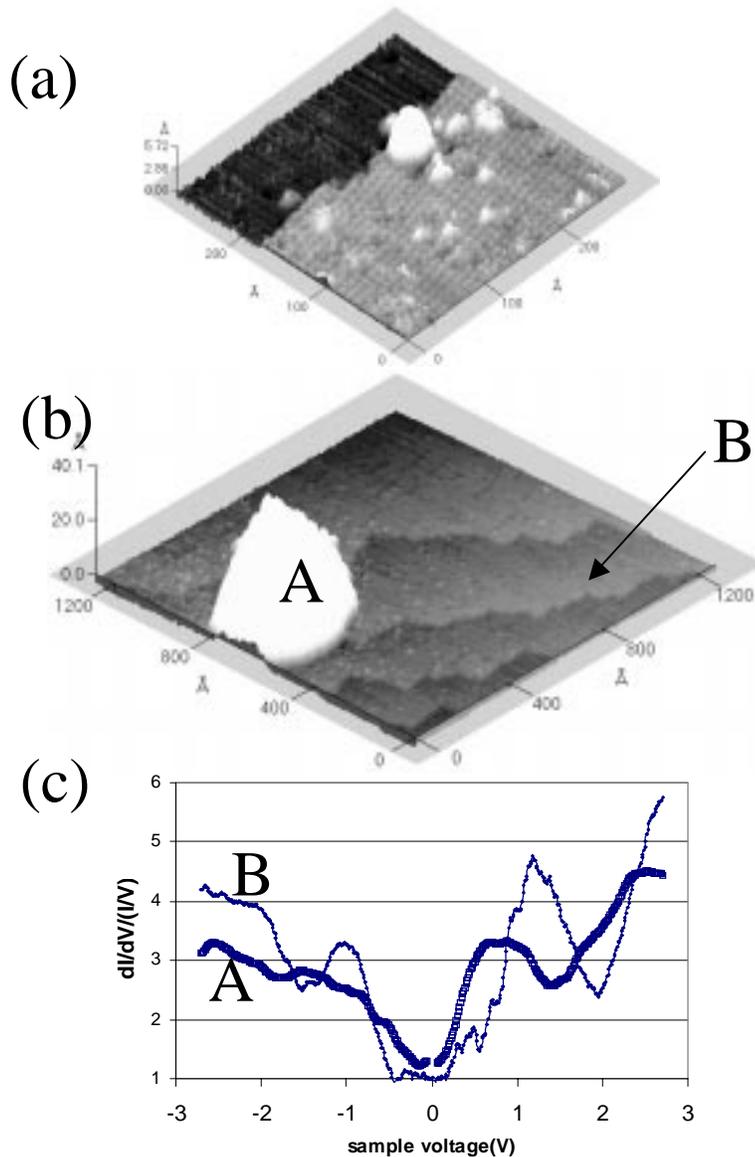


Figure 1(a) 30 nm x 30 nm STM image of a Au dot (diameter  $\sim 3$  nm, height  $\sim 5$  Å) on clean Si(100) surface created by  $-7$  V, 100 ms pulse. (b) 120 nm x 120 nm STM image showing a Au dot made on clean Si (100) surface by  $-10$ V, 100ms pulse. (c) Normalized conductance ( $dI/dV/(I/V)$ ) spectra were measured on the top of dot (A) and on the silicon dimer row region (B) for comparison. While the tunneling IV of the Au dot shows metallic behavior (little or no surface bandgap), that of Si (100) shows typical semiconducting behavior. (We identify the bandgap as the flat region in the normalized conductance where the value is equal to 1.)

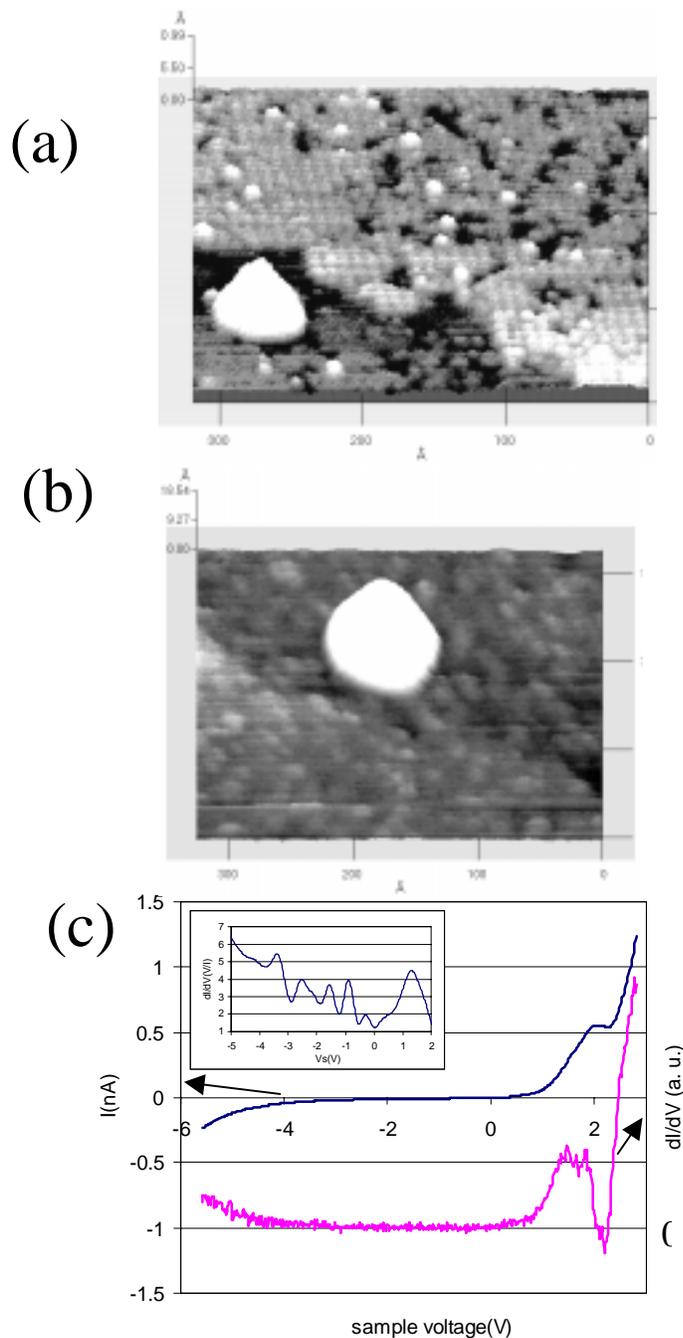
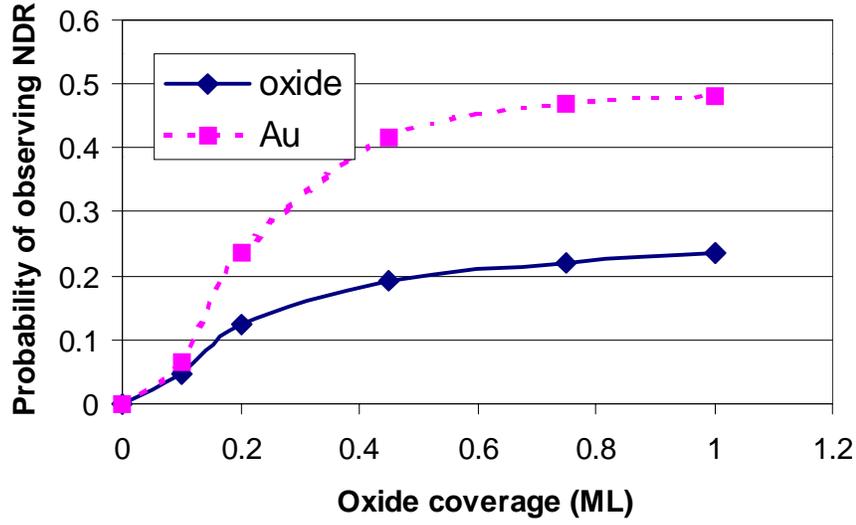
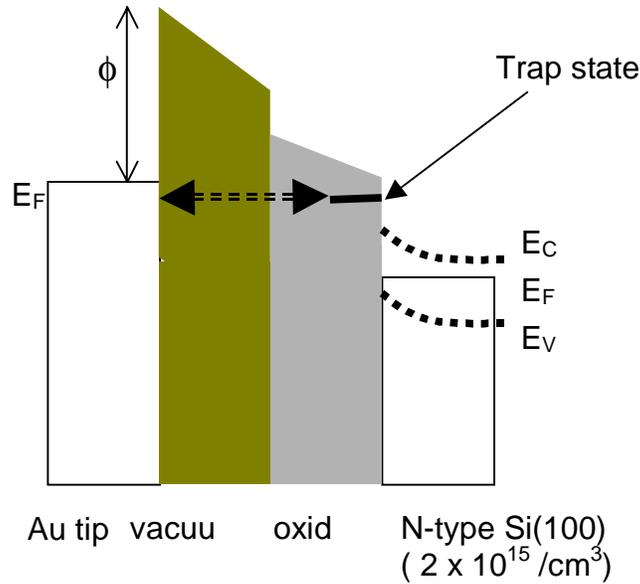


Figure 2 (a) 32 nm x 32 nm STM image of a Au dot (diameter  $\sim 7$  nm, height  $\sim 10$  Å) on 0.2 ML oxidized silicon surface created by  $-8$  V, 100 ms pulse. (b) 32 nm x 32 nm STM image of a Au dot on  $\sim 0.45$  ML oxide (dosing at room temperature, 25 L) created by  $-8$  V, 100 ms pulse. (c) Tunneling IV measured on this dot shows negative differential resistance (NDR) when the sample bias is 2.2 eV. From the normalized conductance ( $dI/dV/(I/V)$ ) this dot also has metallic characteristics.



(a)



(b)

Figure 3(a) The probability of observing NDR at randomly chosen positions on the oxidized surface and on Au dots. (b) Energy band diagram of this configuration (Au coated tip / vacuum / oxide / n-Si (100)). Anomalous tunneling spectroscopy can arise because the captured electron at the localized trap state can act as a Coulomb blockade.